CHAPTER 6

Conducting the Treatability Test

The final PFPR rule allows facilities the choice of achieving zero discharge or complying with the P2 alternative. Zero discharge can be achieved through reuse, off-site disposal of wastewater, or discharge of treated wastewater with pesticide active ingredients at levels below detection.[1] The P2 alternative allows PFPR facilities to discharge their wastewater after implementing listed P2 practices and, in some cases, wastewater treatment. Facilities that treat wastewater to comply with the P2 alternative or to reuse their wastewater must use a technology that provides effective wastewater treatment.

Chapter 4 describes how facilities can use the P2 audit to identify wastewater sources and applicable P2 practices, and make an initial compliance decision for each wastewater source. Chapter 5 describes the most cost-effective wastewater treatment technologies that are demonstrated to reduce the pesticide active ingredients present in PFPR wastewater. Chapter 6 describes the three components of a treatability test and provides guidance to facilities on selecting and testing appropriate wastewater treatment technologies to determine if they are effective for a facility's specific wastewater streams.

Treatability Test Components

- Identification of Wastewater Sources and Treatment Technologies;
- Preparing the Test Plan; and
- Summary and Evaluation of Test Results.

The first component of a treatability test is identifying the wastewater streams that remain after implementation of the P2 practices and require treatment prior to discharge. As discussed in Chapter 4, the facility can use the results of the P2 audit as documented on Table C to identify the sources that will be zero discharge or that will comply with the P2 alternative. As part of this first component, the facility also needs to identify the wastewater technologies appropriate to treat the constituents present in the waste streams requiring treatment (including characteristics that may hinder treatment of the waste streams), and then construct potential treatment trains. Table D, which is described later in this chapter, can be used by facilities to identify the sources that require treatment under the P2 alternative, the constituents in those wastewater sources, and appropriate treatment technology(ies).

Based on this information, the facility can decide whether a treatability test is necessary. A treatability test may be used by a facility to determine whether a particular technology can treat the wastewater, identify analytical or design

[1] If a facility chooses to meet zero discharge through discharge of wastewater with pesticide active ingredients below detection, all pesticide active ingredients that are formulated, packaged, or repackaged at the facility must have analytical methods for use in wastewater.

and operating parameters to act as surrogates for pesticide active ingredient analyses, comply with permitting requirements, or optimize treatment performance.

If a test is warranted, the second component is preparing the test plan. The facility's first step in writing a test plan is determining the size and scope of the test and the sequence of treatment steps. The test plan also specifies the written procedures of how to conduct the test, discusses the design and operating parameters to be evaluated for the specific treatment technologies, determines the equipment and chemicals necessary to conduct the test, and describes the samples to be collected and analyzed (including a discussion of the quality assurance/quality control procedures).

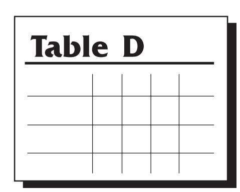
The final component is evaluating the test results, which consists of calculating performance measures, comparing technology results, and evaluating the cost-effectiveness of the individual treatment technologies.

The guidance presented in this chapter for conducting a wastewater treatability test is based on EPA's procedures used during the development of the PFPR effluent limitations guidelines and standards. The treatability test tables discussed in this chapter (Tables D and E) are offered as one way to conduct the test and/or document the test results. It is not required that facilities, permitters, or other auditors use Tables D and E; however, these tables summarize the types of information that are useful in conducting a treatability test. Since it is very difficult to construct one table or checklist with a format useful for all PFPR facilities, EPA considers the tables presented in this manual as a tool to be adapted in whatever way the user feels is appropriate. Example pages of the treatability test tables are shown throughout this chapter to illustrate the types of information captured on the tables. The blank tables are presented in their entirety in Appendix B.

Treatability Test Tables

Table	Title	Purpose
Table D	Identification of Wastewater Sources and Technologies	Helps users list wastewater sources requiring treatment, the potential constituents, and the appropriate treatment technologies.
Table E	Summary and Evaluation of Test Results	Helps users summarize and evaluate the test results for each technology and the final treatment train.

Table D: Identification of Wastewater Sources and Treatment Technologies



Before a treatability test is undertaken, the facility should identify the wastewater sources that require treatment. These sources may include wastewater to be reused in PFPR operations or wastewater to be discharged under the P2 alternative. Table D is the starting point for identifying these sources and the potential treatment technologies to effectively treat them. Completing this table will enable facility personnel to begin identifying the wastewater sources

Table D

Wastewater Sources Requiring Treatment Prior to a P2 Allowable Discharge

Direct Discharge

- All process wastewater.

Indirect Discharge[1]

- Interior equipment rinsate, including drum, bulk tank, and shipping container rinsate;
- Leak and spill cleanup water; and
- Floor wash water.

[1]In individual cases, the requirement of wastewater pretreatment prior to indirect discharge may be removed for floor wash or the final rinse of non-reusable triple rinse by the control authority when pollutant levels are too low to be effectively pretreated and those pollutants do not pass through or interfere with POTW operations.

to include and potential treatment technologies to evaluate in a treatability test. Five steps that can be used to complete Table D and decide whether to conduct a treatability test are detailed below.

Step 1: Identify Wastewater Sources

The user should transfer from Table C to Table D all wastewater sources that will potentially require treatment, prior to either reuse or discharge. In addition, the user should transfer from Table A to Table D a list of the pesticide active ingredients or other constituents present in those wastewater sources. Figure 6-1 presents an example of the types of information transferred while completing this step. The unshaded columns "**Stream Type**", "**Source**", and "**Potential Pollutants**" to illustrate this example.

Table D. Identification of Wastewater Sources and Treatment Technologies

Facility:		**Location:**	
Date:		**Prepared by:**	

Stream Type	Source	Potential Pollutants: Active Ingredients	Potential Pollutants: Other Pollutants	Wastewater Treatment Information: Table 10 Technology[1]	Wastewater Treatment Information: Alternate Treatment Technology[1]	Wastewater Treatment Information: Source for Alternative Technology	Characteristics That Hinder Treatment
1. Shipping Container/ Drum Cleaning - *water or solvent rinses of the containers used to ship raw material, finished products, and/or waste products prior to reuse or disposal of the containers.*	1.a.						
	1.b.						
2. Bulk Tank Rinsate - *cleaning of the interior of any bulk storage tank containing raw materials, intermediate blends, or finished products associated with PFPR operations.*	2.a.						
	2.b.						
3. Formulating Equipment Interior Cleaning - *routine cleaning, cleaning due to product changeover, or special cleaning of the interior of any formulating equipment, including formulation and/or storage tanks, pipes, and hoses. Cleaning materials may include water, detergent, or solvent.*	3.a. *liquid formulation tank # 2*	*Metolachlor Pendimethalin Pyrethrin II*	*BOD_5, TOC, TSS*				
	3.b. *liquid formulation tank # 3*	*Metolachlor Pendimethalin Pyrethrin II*	*BOD_5, TOC, TSS*				
	3.c. *dry formulation tank*	*Linalool Pendimethalin*	*BOD_5, TOC, TSS*				
	3.d.						

1 HD = hydrolysis, AC = activated carbon, PT = precipitation, CO = chemical oxidation, P2 = pollution prevention, OT = other_______________

Figure 6-1. Identifying Wastewater Sources

Step 2: Identify Wastewater Treatment Technologies

Table D

The user should identify treatment technologies that could effectively treat each potential pollutant listed in Step 1. Pollution control technologies for many pesticide active ingredients are presented in Table 10 to Part 455 of the final rule (located in Appendix A). A list of the pesticide active ingredients from Table 10 with their corresponding Shaughnessy codes and CAS numbers is also included in Appendix C. These control technologies include activated carbon adsorption, chemical oxidation, chemical precipitation, hydrolysis, and pollution prevention. EPA selected these technologies based on their applicability to a broad spectrum of pesticides and their relative cost and availability. The user should list the technology for each pesticide active ingredient present in their wastewater in the "**Table 10 Technology**" column.

Appropriate Technologies

- Table 10 listed technology [§455.10(g)]
- Equivalent system [§455.10(h)]
- Pesticide manufacturer treatment system.

Alternate technologies, such as membrane filtration, may also effectively treat pesticide active ingredients present in the facility's wastewater. In specific cases, these other technologies may be more cost-effective than the technologies listed in Table 10 of the rule. Facilities may choose to evaluate these other technologies in a treatability test to determine whether they are equivalent in performance to the Table 10 technologies (Chapter 7 of this manual discusses equivalent technologies in more detail). Facilities may also need to identify treatment technologies for pollutants other than pesticide active ingredients. For example, wastewaters that contain emulsions may require an emulsion breaking pretreatment step before using another technology (e.g., activated carbon adsorption or hydrolysis) to remove pesticide active ingredients. Other wastewaters may require activated carbon adsorption to remove organic priority pollutants in addition to pesticide active ingredients.

If information is not available for a particular pollutant, it may be necessary for the facility to identify a treatment technology based on their knowledge of the pollutant. For example, a technology that is effective on one pesticide active ingredient is often effective on other pesticide active ingredients with similar chemical properties and structures. However, treatment effectiveness should be verified through a treatability test. Table 6-1 provides sources of information on identifying treatment technologies using similarities in chemical properties and structures.

Treatment technologies can be identified from a variety of sources, including technical literature, treatability databases, and treatment vendors. A review of technical literature may reveal information that is not contained in the sources listed in Table 6-1. Treatability testing conducted on similar wastewaters in the PFPR industry or in other industries may provide clues on how to treat a particular wastewater. And treatment technology vendors should have information on the capabilities of their treatment systems. A facility should use all available information as well as knowledge of the various technologies and wastewater to be treated to identify appropriate treatment technologies.

Alternate technologies to treat pesticide active ingredients or other pollutants can be listed in the "**Alternate Wastewater Technology**" column. The source for identification of those alternative technologies (e.g., literature, treatability tests, or other sources) can be specified in the "**Source for Alternative Tech-**

Table 6-1
Sources of Treatment Technology Information

EPA Treatability Database[1]

The U.S. EPA National Risk Management Research Engineering Laboratory in Cincinnati, Ohio maintains a Pesticide Treatability Database that contains information on over 1,600 pesticides that are currently in use in the United States or have been removed from the market in the past 20 years. For each compound, the database contains the following information (where available):

- physical and chemical property data;
- treatability data; and
- Fruendlich isotherm (carbon adsorption) data.

EPA/EAD Treatability Database Report and Addendum[2]

During the development of the PFPR rule, EPA conducted extensive research into the treatment of PAIs, including gathering information from technical literature, analyzing data on treatability tests conducted by PFPR and pesticide manufacturing facilities, sampling existing treatment trains at PFPR and pesticide manufacturing facilities, and conducting bench- and pilot-scale treatability tests. These documents summarize the treatability data collected and describe how treatability data can be transferred to other pesticide active ingredients.

[1]U.S. EPA, Risk Reduction Engineering Laboratory, 26 West Martin Luther King Drive, Cincinnati, OH, 45268

[2]*Final Pesticides Formulators, Packagers, and Repackagers Treatability Database Report* (DCN F7185) and the *Pesticide Formulators, Packagers, and Repackagers Treatability Database Report Addendum* (DCN F7700)

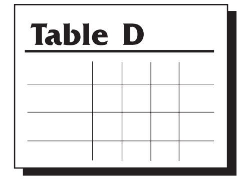
Table D. Identification of Wastewater Sources and Treatment Technologies

Facility: ______________________ **Location:** ______________________
Date: ______________________ **Prepared by:** ______________________

		Potential Pollutants		Wastewater Treatment Information			
Stream Type	**Source**	**Active Ingredients**	**Other Pollutants**	**Table 10 Technology[1]**	**Alternate Treatment Technology[1]**	**Source for Alternative Technology**	**Characteristics That Hinder Treatment**
1. Shipping Container/ Drum Cleaning - *water or solvent rinses of the containers used to ship raw material, finished products, and/or waste products prior to reuse or disposal of the containers.*	1.a.						
	1.b.						
2. Bulk Tank Rinsate - *cleaning of the interior of any bulk storage tank containing raw materials, intermediate blends, or finished products associated with PFPR operations.*	2.a.						
	2.b.						
3. Formulating Equipment Interior Cleaning - *routine cleaning, cleaning due to product changeover, or special cleaning of the interior of any formulating equipment, including formulation and/or storage tanks, pipes, and hoses. Cleaning materials may include water, detergent, or solvent.*	3.a. *liquid formulation tank # 2*	*Metolachlor Pendimethalin Pyrethrin II*	*BOD_5, TOC, TSS*	*AC AC HD*	*HD*	*Treatability testing, Literature*	
	3.b. *liquid formulation tank # 3*	*Metolachlor Pendimethalin Pyrethrin II*	*BOD_5, TOC, TSS*	*AC AC HD*	*HD*	*Treatability testing, Literature*	
	3.c. *dry formulation tank*	*Linalool Pendimethalin*	*BOD_5, TOC, TSS*	*AC AC*	*HD*	*Treatability testing, Literature*	
	3.d.						

1 HD = hydrolysis, AC = activated carbon, PT = precipitation, CO = chemical oxidation, P2 = pollution prevention, OT = other______________________________

Figure 6-2. Identifying Wastewater Treatment Technologies



nology” column. Figure 6-2 presents an example of the types of information collected when completing Step 2. The unshaded columns under **“Wastewater Treatment Information”** illustrate this example.

Step 3: Identify Characteristics That Hinder Treatment

Throughout the pesticide industry, many products may be formulated, packaged, or repackaged using different types of equipment. This variety in products and equipment results in variable wastewater characteristics, which in turn affects the treatability of those wastewaters. For example, a wastewater with a high amount of organic compounds may be difficult to treat with chemical oxidation, as the organic compounds may compete with the pesticide active ingredients for the available oxidizing agent.

The application of treatment technologies to variable PFPR wastewater must be tailored to the specific characteristics of the wastewater. Table 6-2 presents some wastewater characteristics that may interfere with emulsion breaking, activated carbon adsorption, hydrolysis, chemical oxidation, and chemical precipitation technologies; however, these characteristics do not necessarily preclude use of the technology. The degree to which a wastewater exhibits a characteristic will affect the degree to which the technology is adversely affected. In many cases, a wastewater displaying an adverse characteristic can still be effectively treated through modifications of the treatment technology or the addition of a pretreatment step. For example, a wastewater may be difficult to treat using activated carbon adsorption if it has a high suspended solids content, because the suspended solids may plug the carbon column. However, it may be possible to remove the suspended solids through settling or filtration before activated carbon treatment.

Table 6-2
Wastewater Characteristics That Adversely Impact Treatment Effectiveness

	Technology				
Wastewater Characteristic	**Emulsion Breaking**	**Activated Carbon Adsorption**	**Hydrolysis**	**Chemical Oxidation**	**Chemical Precipitation**
Organics		✔		✔	
Suspended Solids		✔		✔	
Buffered Solution	✔		✔		✔
Temperature		✔			✔
pH		✔		✔	
Detergents/ Surfactants	✔	✔		✔	✔
Oil and Grease		✔		✔	

The most common pretreatment technologies used for PFPR wastewaters are settling, filtration, emulsion breaking, chemically assisted clarification, neutralization, and ultrafiltration. Table 6-3 lists the types of wastewater characteristics that can be effectively treated by these pretreatment methods. EPA conducted treatability tests to evaluate emulsion breaking, chemically assisted clarification, and ultrafiltration as part of the development of the PFPR rule. See Chapter 5 for more information on these technologies.

Table 6-3
Pretreatment Technologies for Adverse Wastewater Characteristics

	Technology					
Wastewater Characteristic	**Settling**	**Filtration**	**Emulsion Breaking**	**Neutralization or pH Adjustment**	**Chemical Assisted Clarification**	**Ultrafiltration**
Organics			✔		✔	✔
Suspended Solids	✔	✔	✔		✔	✔
Buffered Solution				✔		
pH				✔		
Detergents/ Surfactants			✔		✔	✔
Oil and Grease			✔		✔	✔

Wastewater characteristics that hinder treatment can be listed in the "**Characteristics That Hinder Treatment**" column of Table D. Figure 6-3 presents an example of the types of information that may be documented during the completion of Step 3.

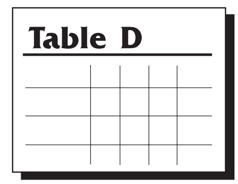


Table D. Identification of Wastewater Sources and Treatment Technologies

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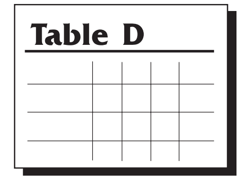
	1.b.						
2. Bulk Tank Rinsate - *cleaning of the interior of any bulk storage tank containing raw materials, intermediate blends, or finished products associated with PFPR operations.*	2.a.						
	2.b.						
3. Formulating Equipment Interior Cleaning - *routine cleaning, cleaning due to product changeover, or special cleaning of the interior of any formulating equipment, including formulation and/or storage tanks, pipes, and hoses. Cleaning materials may include water, detergent, or solvent.*	3.a. *liquid formulation tank # 2*	*Metolachlor Pendimethalin Pyrethrin II*	*BOD_5, TOC, TSS*	*AC AC HD*	*HD*	*Treatability testing, Literature*	
	3.b. *liquid formulation tank # 3*	*Metolachlor Pendimethalin Pyrethrin II*	*BOD_5, TOC, TSS*	*AC AC HD*	*HD*	*Treatability testing, Literature*	
	3.c. *dry formulation tank*	*Linalool Pendimethalin*	*BOD_5, TOC, TSS*	*AC AC*	*HD*	*Treatability testing, Literature*	*High solids content*
	3.d.						

1 HD = hydrolysis, AC = activated carbon, PT = precipitation, CO = chemical oxidation, P2 = pollution prevention, OT = other________________________________

Figure 6-3. Identifying Characteristics That Hinder Treatment



Step 4: Construct Potential Treatment Trains

Often the wastewater at a PFPR facility contains more than one pesticide active ingredient and may also have characteristics that require a pretreatment step. In these situations, several technologies may be necessary to completely treat the wastewater. These technologies can be used in series in what is called a treatment train.

For example, a facility generates wastewater from floor washing that contains several pesticide active ingredients, including atrazine, metolachlor, and copper naphthanate. In order to effectively treat this wastewater, the facility may construct a treatment train, shown in Figure 6-4, which consists of emulsion breaking to remove oil and grease and suspended solids picked up from the floor during floor washing, chemical precipitation to remove the copper naphthanate, hydrolysis to treat the atrazine, and activated carbon adsorption to remove the metolachlor and other priority pollutants contained in the wastewater.

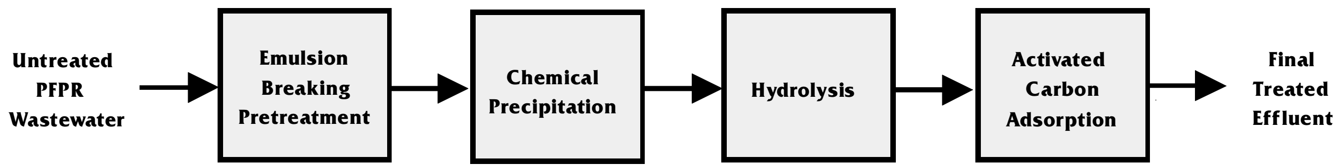


Figure 6-4. Example Treatment Train

When conducting a treatability test, facilities may only test the individual unit operations. However, if a facility intends to implement the entire treatment train, testing the entire train may reveal important information about how the wastewater characteristics change with each treatment step. Testing the wastewater through the entire treatment train can help troubleshoot the system and determine whether pretreatment steps are adequate to prevent malfunctioning of other unit operations in the treatment train.

Step 5: Determine Whether to Conduct a Treatability Test

After identifying wastewater streams that require treatment and the appropriate technologies for the constituents in those streams, a facility should determine whether a test is warranted for their circumstances. Several factors should be considered in making this determination. A treatability test can help a facility to evaluate whether the selected technologies effectively treat their wastewater and whether additional treatment steps are necessary. If a facility chooses technologies different from the ones listed in Table 10 of the final rule for the treatment or removal of pesticide active ingredients, a treatability test can be used to demonstrate that treatment is equivalent (demonstration of equivalent treatment is discussed more fully in Chapter 7). The test can also be used to determine the optimum treatment conditions, or may be required by permit writers or control authorities to evaluate treatment effectiveness before they allow PFPR wastewater to be discharged.

WHY CONDUCT A TREATABILITY TEST?

- Find out what technologies work best for your wastewater and optimize treatment performance.
- Show that an alternative technology is equivalent to a technology listed in Table 10 to Part 455.
- Meet the requirements of your NPDES permit writer or control authority prior to discharging PFPR wastewater.
- Identify surrogate parameters as an alternative to traditional laboratory analysis.

A treatability test may also allow a facility to identify surrogate parameters (e.g., total organic carbon) that will indicate the treatment effectiveness of their system without analyzing the wastewater for each individual constituent. Because of the number of pesticide active ingredients handled by some facilities, surrogate parameters can reduce the analytical costs associated with compliance. In addition, EPA-approved methods do not exist for all pesticide active ingredients, while other chemicals may be difficult to quantify because contaminants in the wastewater interfere with the analysis; in these cases, surrogate parameters allow some measure of treatment effectiveness to be quantified. To use surrogate parameters for any of these reasons, a facility may be required to perform a treatability test to establish the relationship between the surrogate parameter and the constituents it is meant to represent. The use of surrogates is not required by the rule.

Preparing The Test Plan

Once the decision to conduct a treatability test is made, the facility should prepare a written test plan. A test plan contains a set of predetermined procedures designed to ensure the test's success. The test plan helps facility personnel organize and prepare for the test, ensure that the test is conducted properly, provide documentation of the test, and troubleshoot treatment systems and procedures.

The test plan should have sufficiently detailed and clearly written instructions so that treatment system operators can easily conduct the test as specified. The plan should first of all clearly state the goals that are to be accomplished through performing the treatability test and the technologies to be evaluated. The plan should then delineate the size of the test, the target design and operating parameters for each treatment step, detailed instructions on how to perform each treatment step (including who is to perform the action, when the action should be performed, and the equipment and materials to be used), and sampling and analysis procedures.

Components of the Treatability Test Plan

- Goals of test and the treatment technologies to be evaluated (including the sequence of treatment steps);
- Size of the test;
- Target design and operating parameters;
- Written instructions for each step of the test, including the date, time, location, and personnel involved in the test;
- Equipment and materials required for the test; and
- Sampling plan specifying sample points, times, and procedures, sample analyses, sample preservation and shipping, and quality assurance/quality control procedures.

After the goals of the test are set, the facility can follow the following five steps in preparing a test plan for conducting a treatability test.

Step 1: Determine the Size of the Test

Full-scale treatment systems at PFPR facilities vary in size from very small systems (treating 100 gallons or less per year) to very large systems (treating millions of gallons per year). When performing a treatability test, it is not always necessary to treat a large volume of wastewater, and often valuable information can be acquired from smaller scale tests. Treatability tests are typically categorized based on size as bench-, pilot-, and full-scale tests.

A bench-scale test is useful to screen treatment technologies or determine initial design and operating parameters, and is typically conducted on one gallon or less of wastewater. Bench-scale tests use laboratory equipment (e.g., beakers, hot plates, and stirring rods), and may be conducted on synthetic wastewater (i.e., distilled water spiked with a known concentration of contaminant). A bench-scale test requires less cost and effort because of the smaller volume of wastewater tested and the basic equipment used. In addition, a bench-scale treatability test may involve less sophisticated sampling and analysis, and may use indicator parameters (e.g., turbidity) or visual appearance of the wastewater instead of laboratory analysis to gauge test results.

A pilot-scale test is conducted on actual wastewater, and is used to optimize design and operating parameters and to troubleshoot treatment problems before constructing a full-scale treatment system. Actual wastewater may contain surfactants, inerts, solvents, or other impurities that may interfere with treatment. The test is intermediate in size, although for many PFPR facilities that generate small volumes of wastewater, a pilot-scale system is equivalent in size to a full-scale system. Pilot-scale tests typically use smaller and simpler equipment than would be found in a full-scale system, such as buckets or drums instead of treatment tanks; portable mixers and pumps instead of built-in mixers and pumps; and flexible hoses instead of hard piping. These systems may also use temporary equipment that can be placed in storage or disposed of after the test instead of permanently installed equipment.

A full-scale treatability test is conducted on actual wastewater using the actual size and type of equipment to be used for routine treatment.

Step 2: Determine the Design and Operating Parameters

The effectiveness of a treatment step is related to certain design and operating parameters that determine how well the treatment system functions. The specific design and operating parameters differ for each type of technology. Table 6-4 presents a list of common parameters used for wastewater treatment technologies. For the treatment of PFPR wastewater, design and operating parameters typically include the amount of chemicals and/or materials used, temperature, pH, and wastewater flow rates.

Table 6-4
Common Design and Operating Parameters

- Temperature
- pH
- Pressure
- Treatment time
- Flow rate
- Amount of treatment chemicals/materials
- Mixing
- Visual appearance of wastewater

Usually, a treatment technology will operate within a range of design and operating parameters. The point within that range at which the treatment system performance and cost are optimized will depend on site-specific factors such as wastewater characteristics and volume.

Prior to the treatment test, target design and operating parameters appropriate for each treatment technology should be identified in the test plan. Because it is difficult to control some parameters precisely, a range of values (e.g., pH 2 to 12) to be evaluated during the test should also be identified. During the treatability test, treatment system operators should record the actual design and operating parameter values to identify at what values the optimum treatment performance of the system was achieved.

➡ Identify relevant design and operating parameters

Treatment technologies for PFPR wastewaters use a variety of mechanisms to achieve treatment. These mechanisms include physical separation of contaminants from wastewater, chemical reactions, phase separations, or a combination. With each technology, a unique set of design and operating parameters relevant to that technology needs to be monitored to ensure that the treatment technology is functioning properly. In some cases, the relevant design and operating parameters to be monitored may depend upon the specific characteristics of the wastewater to be treated as well as the treatment technology.

Table 6-5 presents the design and operating parameters that are typically monitored for the five technologies used by EPA in developing industry compliance costs for the PFPR rule. These technologies are described more fully in Chapter 5. Design and operating parameters are listed for these technologies because they are the technologies that are most frequently used in on-site

Table 6-5
Treatment Technology Design and Operating Parameters

Activated Carbon Adsorption Parameters

- Wastewater flow rate
- Type and amount of carbon used
- Saturation loading
- Temperature
- pH
- Carbon bed dimensions

Chemical Oxidation Parameters

- Temperature
- pH
- Amount and type of chemicals added
- Free chlorine, peroxide, or other chlorinating agent concentration
- Treatment time or wastewater flow rate

Precipitation Parameters

- Temperature
- pH
- Amount and type of chemicals added
- Mixing
- Treatment time or wastewater flow rate

Emulsion Breaking Parameters

- Temperature
- pH
- Mixing
- Amount and type of chemicals added
- Turbidity

Hydrolysis Parameters

- pH
- Temperature
- Mixing
- Amount and type of chemicals added
- Treatment time or wastewater flow rate

treatment of PFPR wastewaters and are the technologies for which EPA has the greatest amount of information. Note that these are not the only treatment technologies that can be successfully applied to PFPR wastewaters. In some cases, facilities may wish to monitor other design and operating parameters in addition to the ones listed in Table 6-5. Technical literature on the selected technology to be tested and previous wastewater treatability tests can help in identifying relevant operating parameters.

➡ Select design and operating parameter values

After identifying the appropriate design and operating parameters, facilities should set a range of values to be evaluated during the test. These values can be estimated from several sources:

- Previous treatment tests on the same or similar chemicals or wastewaters;
- Technical literature on the treatment technology; and
- Technology vendors.

The first time a wastewater is treated through a particular technology, PFPR facilities may wish to set the target design and operating parameter values at conservative levels that will overtreat the wastewater. Because PFPR wastewaters tend to be highly variable, and equipment and procedures may also vary from test to test, a parameter value that proved to be effective in previous tests on different wastewaters may not be an appropriate value for a specific facility's wastewater. By setting conservative parameter values during an initial test, facilities will not wrongly conclude that a particular treatment technology is ineffective when all that is necessary to achieve effective treatment is to adjust the design and operating parameter values.

For example, if technical literature indicates that a chemical oxidation time of six hours will effectively treat a chemical, a PFPR facility conducting an initial treatability test may wish to perform chemical oxidation for 8 or 12 hours. By sampling the wastewater at one- or two-hour intervals, the facility can ensure that effective treatment occurs during the test while also identifying how much treatment time is needed for their particular wastewater.

➡ Optimize treatment performance through design and operating parameters

Once a facility has performed a treatability test and identified an effective technology, the design and operating parameters used in that test can be used as a basis for future testing, provided the wastewater characteristics do not significantly change. However, facilities may wish to increase treatment performance, decrease treatment time, and reduce the cost of treatment. By optimizing design and operating parameters, facilities can achieve these objectives.

A properly run and well-documented treatability test will give indicators as to how to optimize treatment system performance. By reviewing the design and operating parameters achieved during treatability testing in conjunction with treatment system operator observations and laboratory analyses, facilities can determine what changes are likely to result in treatment system optimization.

By reviewing the design and operating parameter measurements, adjustments can be made either during the treatability test or in subsequent tests to optimize performance. In some cases, facilities can monitor design and operating parameters instead of using costly laboratory analyses to verify treatment effectiveness. For example, facilities can monitor the pH, temperature, and treatment time for a hydrolysis unit instead of having the treated wastewater analyzed to verify that hydrolyzable chemicals are removed. However, substituting laboratory analyses with design and operating parameter monitoring to demonstrate compliance will ultimately need to be approved by the control authority. Occasional laboratory analyses may be required to confirm that design and operating parameter monitoring accurately predicts treatment effectiveness.

If one of the goals of a treatability test is to optimize the treatment system, the facility may choose to monitor design and operating parameters and sample the system for laboratory analyses more frequently than is necessary to determine treatment system performance. For example, during an emulsion breaking pretest, the facility may collect samples under both acidic and alkaline conditions or at various temperatures to determine what conditions result in the greatest degree of separation. Facilities may also optimize treatment system performance by changing wastewater management methods. For example, by segregating certain wastewaters with characteristics that make them hard to treat, treatment system performance can be improved. In some cases, exterior equipment cleaning or floor wash water may contribute large amounts of suspended solids to a wastewater. By segregating the floor wash and exterior cleaning waters from other wastewaters, the facility may eliminate the need for emulsion breaking or other pretreatment for nonexterior waters, thereby reducing the cost of pretreatment by reducing the volume of wastewater requiring pretreatment. Alternatively, the facility may find that it is less expensive to dispose of some wastewaters than to treat them. For example, off-site disposal of floor wash water may cost less for some facilities than adding an emulsion breaking step to a treatment train.

As discussed in Chapter 7, the final PFPR rule requires that facilities choosing the P2 alternative must demonstrate, as part of their on-site compliance paperwork, that the treatment technologies they are choosing are well-operated and maintained. By documenting the optimal design and operating parameters that reflect the appropriate level of treatment for each treatment technology, a facility can demonstrate that its treatment system is well-operated and maintained. The section of this chapter on evaluation of test results and Chapter 7 discuss how Tables D and E can provide the documentation for demonstrated effectiveness of a facility's treatment system.

Step 3: Prepare Detailed Instructions

Clear and detailed written procedures will not only help ensure that treatability testing is successful, but can also help in troubleshooting treatment systems that are not performing as well as expected and in optimizing treatment performance. See the references listed at the end of Chapter 5 and/or the example in Appendix D for descriptions of treatability test procedures used for EPA-sponsored tests.

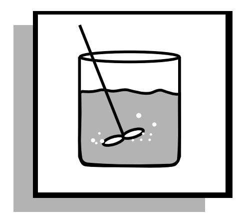
If a treatability test shows poor results, a review of the test plan, deviations from the test plan, and observations made during the treatability test may help identify whether the poor results are due to test procedures or whether the selected treatment technology is not appropriate for the wastewater being treated. This review can also help facilities determine whether additional pretreatment is necessary to allow treatment technologies to function properly.

Step 4: Identify Equipment and Chemicals

Equipment and chemicals are necessary in conducting the treatability test, collecting and analyzing the samples, and monitoring the design and operating parameters. When performing a treatability test, the equipment used should be cleaned to avoid introducing outside contaminants that may skew test results. Facilities should also use equipment constructed of materials that are compatible with the wastewater, contaminants, and treatment chemicals to be used in the test.

The types and sizes of equipment and chemicals needed to perform treatability tests to evaluate emulsion breaking, hydrolysis, activated carbon adsorption, chemical oxidation, and chemical precipitation are discussed below. These technologies, described in Chapter 5, are the most cost-effective technologies that remove or destroy pesticide active ingredients and priority pollutants in PFPR wastewater.

➡ Emulsion Breaking



Facilities performing an emulsion breaking test should use a tank sized for the volume of wastewater to be tested. If the tank has an open top, the facility should cover the tank to minimize evaporative and heat losses. If the tank does not have graduated markings, an additional container may be necessary to measure the volume of the wastewater. A pump may also be required to transfer the wastewater to and from the tank.

Acid lowers the pH of the wastewater and encourages emulsion breaking. A variety of acids can be used for this purpose, including sulfuric and hydrochloric acid. To further encourage emulsion breaking, the facility may heat the wastewater in the tank. Heating equipment includes hot plates, electric band heaters, immersion heaters, and steam jackets.

Emulsion breaking also requires stirring to mix treatment chemicals and to encourage the breaking of the emulsion. Rapid and turbulent mixing may be used initially to mix the treatment chemicals, but may cause contaminants to remain emulsified in the wastewater if used throughout the test. It is recommended that the facility use low-speed mixing and low-shear mixers such as paddle mixers.

The pH of the wastewater can be determined with disposable pH strips or with an electronic pH meter. The temperature of the wastewater can be determined with a thermometer or with a thermocouple. The facility may also wish to neutralize the pH of the wastewater after emulsion breaking if other portions of the treatment train are not compatible with a low pH.

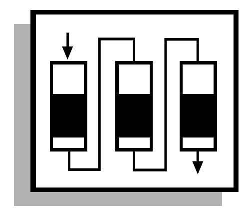
➡ Hydrolysis

Facilities performing a hydrolysis test should use a tank sized for the volume of wastewater to be tested. If the tank has an open top, the facility may cover the tank to minimize evaporative and heat losses. If the tank does not have graduated markings, an additional container may be necessary to measure the volume of the wastewater. A pump may be required to transfer the wastewater to and from the tank, and a mixer is typically used during hydrolysis to homogenize the wastewater.

Hydrolysis reactions typically occur more rapidly in acidic or basic environments. A variety of bases and acids are acceptable to raise or lower the pH of the wastewater. To further encourage the hydrolysis reaction, the facility may heat the wastewater in the tank. Heating equipment includes hot plates, electric band heaters, immersion heaters, and steam jackets.

The pH of the wastewater can be determined with disposable pH strips or with an electronic pH meter. The temperature of the wastewater can be determined with a thermometer or with a thermocouple. The facility may choose to neutralize the wastewater after the treatability test; a variety of acids and bases can be used for this purpose.

➡ Activated Carbon Adsorption

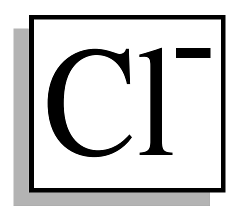


Facilities performing an activated carbon adsorption test must use a carbon bed or column sized for the volume of wastewater to be tested. Flexible tubing or hard piping may be used to convey water to the column and remove treated wastewater. The facility will need a pump to move the wastewater through the bed or column. Many carbon treatment systems use several beds in series. As the first bed becomes saturated, it is removed from the system. The influent is then directed to the second bed in the series, and an additional bed is added to the end of the series to replace the saturated bed that was removed.

The facility may use prefilled carbon beds from a vendor or prepare its own bed or column. If the facility is packing a carbon bed or column itself, it will be necessary to prepare the carbon. A scale should be used to weigh the carbon used to pack the column. It may also be necessary to rinse the carbon to remove fines and to deaerate the carbon.

The pH of the wastewater can be determined with disposable pH strips or with an electronic pH meter. The temperature of the wastewater can be determined with a thermometer or with a thermocouple.

➡ Chemical Oxidation (Alkaline Chlorination)

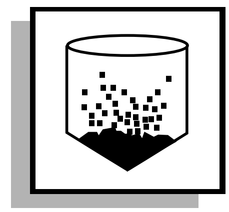


Facilities performing a chemical oxidation test via alkaline chlorination should use a tank sized for the volume of wastewater to be tested. If the tank has an open top, the facility may cover the tank to minimize evaporative and heat losses. If the tank does not have graduated markings, an additional container may be necessary to measure the volume of the wastewater. A pump may be required to transfer the wastewater to and from the tank. An electric mixer or a magnetic stirring bar is typically used to mix the wastewater during chemical oxidation.

Chemical oxidation occurs more readily in an alkaline environment. While a variety of bases are acceptable, sodium hydroxide is most commonly used to raise the pH of the wastewater. A variety of chlorine-containing chemicals are available to initiate chlorination; sodium hypochlorite is commonly used during chemical oxidation. A facility may choose to neutralize the wastewater with an acid following treatment, or add sodium thiosulfate or other free chlorine scavenger following treatment to reduce residual free chlorine in the wastewater.

The pH of the wastewater can be determined with disposable pH strips or with an electronic pH meter. The temperature of the wastewater can be determined with a thermometer or with a thermocouple. The level of free chlorine or other oxidant can be determined using readily available test kits. Facilities should contact laboratory equipment vendors for information on such test kits.

➟ Chemical Precipitation (Sulfide Precipitation)



Facilities performing a chemical precipitation test should use a tank sized for the volume of wastewater to be tested. If the tank does not have graduated markings, an additional container may be necessary to measure the volume of the wastewater. A pump may be required to transfer the wastewater to and from the tank.

A facility can use a variety of chemicals to initiate sulfide precipitation, including sodium sulfate. Mixing the wastewater will encourage flocculation of the metal precipitates. Although rapid and turbulent mixing may be used initially to mix the treatment chemicals, such mixing may cause precipitates to deflocculate. It is recommended that the facility use low-speed mixing and low-shear mixers such as paddle mixers. A filter or vacuum pump may be used to remove the flocculated solid particles from the wastewater, or the facility may decant the wastewater.

The pH of the wastewater can be determined with disposable pH strips or with an electronic pH meter. The temperature of the wastewater can be determined with a thermometer or with a thermocouple.

Step 5: Prepare the Sampling Plan

During and after the test, the facility will need to sample the wastewater to ensure that the technology selected to treat the wastewater is performing adequately. Prior to the start of the test, the facility should prepare a sampling plan to describe the planned data collection, field measurements, and sample analyses. Table 6-6 lists the main components of a comprehensive sampling plan.

Table 6-6
Components of a Sampling Plan

- Selection of sampling points;
- Field measurements and operating parameters;
- Sample analyses;
- Sample preservation and shipping; and
- Quality assurance/quality control.

➟ Select Sampling Points

Facility-specific sampling points should be identified so that the samples collected will represent the following types of streams:

- Influent to the treatment system (e.g., commingled wastewater from PFPR operations and pretreatment steps);
- Influent to the individual treatment units;

- Effluent from individual treatment units (e.g., hydrolysis effluent); and
- Final effluent from the treatment system.

Sample point selection should be designed for the specific system. Typically, wastewater samples are collected from the influent and effluent of each treatment unit operation to evaluate the performance of the individual unit. The initial influent and final effluent samples from the whole treatment system are collected to evaluate the system's overall performance.

If the facility chooses to investigate whether individual wastewater streams (e.g., floor wash) require pretreatment, the selected sampling points should include those individual raw wastewater streams. The commingled influent to the treatment system would then consist of the pretreatment unit effluent and the raw wastewater streams that do not require pretreatment.

The facility may also wish to collect multiple samples during a treatment step to better calculate technology-specific performance measures (described in the Evaluation of Test Results section). Table 6-7 presents examples of the sampling frequency and analysis that might be performed for various technologies on a pilot scale. Sample frequency should account for the variability of the wastewater generated from the various processes at the facility.

Table 6-7
Example Sample Collection for Pilot-Scale Study

Technology	Performance Measure	Sampling Frequency	Typical Sample Analyses
Any technology	Destruction and removal efficiency	Collect influent and final effluent samples	Any constituent
Activated Carbon	Carbon breakthrough curve	Collect effluent samples after every 60 liters has passed through the carbon bed	Pesticides Organics Total organic carbon
Activated Carbon	Saturation loading/carbon isotherm	Treat a set volume (e.g., one liter) of wastewater through varying amounts of carbon and collect effluent samples	Pesticides Organics Total organic carbon
Emulsion Breaking	Time for phase separation	Visually inspect samples hourly for phase separation	Turbidity Total suspended solids Oil and grease
Hydrolysis	Half-life calculation	Collect effluent samples every 2-6 hours of treatment	Pesticides

➡ Field Measurements and Operating Parameters

As part of the test documentation, facilities should prepare field logs for each sample point. Typically, these logs will contain the types of information listed in Table 6-8 and be included in the report documenting the test results.

Typical field sampling equipment includes pH meters or indicator paper, thermometers, scoops or shovels, and bottle dippers. Noncontaminating pH indicator papers are often used during sampling and preservation; however, if a more precise pH determination is required, a pH meter, calibrated each day in the field, can be used. The pH electrode should be decontaminated prior to sampling by rinsing the probe in deionized water. Temperature can be measured from either an aliquot collection jar or from the process stream after sample collection to ensure that the thermometers do not contaminate samples. Other sampling equipment that directly contacts the sample, such as scoops, shovels, and bottle dippers, should be precleaned and dedicated to each sample point or cleaned prior to reuse. Table 6-9 lists the typical decontamination procedures for sample collection containers.

Table 6-8
Typical Field Log Data

- Sampling point description;
- Date and time of sample collection;
- Name or initials of sampler;
- Deviations from the sampling plans or test plan;
- Field measurements;
- Flow data;
- Production data;
- Observations; and
- Other comments.

➡ Sample Analyses

Wastewater samples may be analyzed for conventional and selected nonconventional parameters, priority pollutants, and nonpriority organic and metal pollutants. For the PFPR industry, the notable nonconventional pollutants expected to contribute a significant toxic loading to PFPR facility wastewaters are the pesticide active ingredients used in formulating, packaging, or repackaging operations. PFPR wastewater may also contain specific organic and metal pollutants used in the facility's pesticide formulations or high levels of oils or solids.

Table 6-9
Decontamination Procedures

For samples in which inorganic constituents are to be analyzed, the following decontamination procedures are effective:

- Wash in a nonphosphate detergent and water solution;
- Rinse with dilute hydrochloric acid;
- Rinse with tap water; and
- Rinse with Type II reagent grade water.

For samples in which organic constituents are to be analyzed, the following decontamination procedures are effective:

- Wash with detergent;
- Rinse with tap water;
- Rinse with distilled water;
- Rinse with acetone; and
- Rinse with laboratory-grade hexane.

Equipment blanks should be collected as necessary to verify adequate decontamination procedures.

At a minimum, samples should be analyzed for the facility's pesticide active ingredients (if a method is available) and for priority pollutants. A number of pesticide active ingredient methods can be found in the *Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater* (EPA 821-R-93-010). It is also helpful to analyze the samples for the classical wet chemistry parameters listed in Table 6-10. These parameters can sometimes be correlated to the level of treatment achieved during a particular unit operation. For example, total organic carbon (TOC) is often used as an indicator for activated carbon adsorption. During a treatability test or during an initial monitoring period for a full-scale treatment system, the samples should be analyzed for both TOC and the specific pesticide active ingredients. If the test results show a correlation between the two, then TOC can be used as a surrogate monitoring parameter during normal treatment operations. If metals are not used in the facility's operations, samples for metals analyses may be collected only at the treatment system influent and the final effluent to evaluate the overall system removals for those constituents.

Facilities may also wish to analyze the samples for other parameters that may affect the performance of the selected treatment technologies. For example, a treatability test for activated carbon might include analysis of total suspended solids, since solids can plug the carbon bed and reduce overall performance of the system.

Different types of analyses are conducted using separate analytical methods that have specific preservation methods. These analyses may also be conducted by separate laboratories. As a result, wastewater collected at each sample point is separated into one or more containers, called a sample "fraction," for each analysis or set of similar analyses. A comprehensive water sample set typically consists of the eight fractions listed in Table 6-11. The pesticide active ingredients analyzed will be facility-specific. Some pesticides are analyzed by the same method; a separate pesticide fraction is required for each analytical method. As mentioned previously, it may not be necessary for the facility to analyze the wastewater for all parameters.

Table 6-10
Classical Wet Chemistry Parameters

- Ammonia as nitrogen;
- Biochemical oxygen demand (BOD);
- Chemical oxygen demand (COD);
- Cyanide, total;
- Fluoride;
- Hexane extractable material (HEM);
- Nitrate/nitrite nitrogen;
- pH;
- Total dissolved solids (TDS);
- Total organic carbon (TOC); and
- Total suspended solids (TSS).

➡ Sample Preservation

Individual sample fractions must be preserved according to the appropriate analytical method. Table 6-12 lists the typical analytical fractions, along with the typical sample volume, sample container, and on-site preservation for each fraction.

Sample volume, container type, preservation, and storage requirements for each analytical method are specified in the *Handbook for Sampling and Sample Preservation of Water and Wastewater* (EPA-600/4-82-029). During sample collection, facilities should follow good housekeeping and health and safety practices by avoiding cross-contamination of samples and leaks and spills.

Table 6-11
Typical Sample Fractions

- Specific pesticide active ingredient(s);
- Volatile organic pollutants;
- Semi-volatile organic pollutants;
- Metals;
- Group I classical parameters (BOD, TSS, TDS, pH, and fluoride);
- Group II classical parameters (TOC, COD, ammonia nitrogen, nitrate/nitrite nitrogen);
- Hexane extractable material; and
- Total cyanide.

Table 6-12
Typical Sample Fractions and Preservation

Sample Fraction	Sample Volume	Sample Container	On-Site Preservation
Typical Pesticide Method	2 Liters	1 Liter Amber Narrow-Mouth Glass	4°C; pH 5-7 with NaOH or HCl
Volatile Organics	80 mL	40 mL VOA Vial	4°C
Semivolatile Organics	2 Liters	1 Liter Amber Narrow-Mouth Glass	4°C
Metals	1 Liter	1 Liter Narrow-Mouth Plastic	pH 2 with HNO_3
Group I Parameters[1]	1 Liter	1 Liter Narrow-Mouth Plastic	4°C
Group II Parameters[2]	1 Liter	1 Liter Narrow-Mouth Glass	4°C; pH 2 with H_2SO_4
Total Cyanide	1 Liter	1 Liter Narrow-Mouth Plastic	4°C; pH 12 with NaOH
Hexane Extractable Material	1 Liter	1 Liter Wide-Mouth Glass	4°C; pH 2 with HCl

[1]Group I parameters include BOD_5, pH, fluoride, TDS, and TSS.

[2]Group II parameters include ammonia nitrogen, nitrate/nitrite nitrogen, COD, and TOC.

➡ Quality Assurance/Quality Control

To ensure the accuracy of the data collected during the treatability test, it is critical that proper quality assurance/quality control (QA/QC) procedures be followed throughout the entire treatability test and during sampling and analysis. The sample plan should identify the following three components of the facility's QA/QC plan:

(1) Specify procedures to ensure that data quality is within prescribed limits of acceptability;

(2) Provide QC data that may be used to assess data quality in terms of precision and accuracy; and

(3) List analytical methods to be used.

Appropriate QA/QC procedures should be followed by the facility and the laboratory that the facility selects to analyze the samples.

For example, when collecting samples, the facility should also collect QA/QC samples, including field duplicate samples, field blanks, equipment blanks, and trip blanks.

- Field duplicate samples are two successive samples from the same sampling point. Results of the field duplicate analyses are used to evaluate overall precision and cover all sources of data variability, including sample collection, handling, preparation, and analysis. Field duplicates are submitted to the laboratory as blind duplicates.
- Field blanks are samples of an analyte-free matrix (e.g., HPLC water), which are prepared at the sampling site by pouring the HPLC water directly into the sample bottles. Results are used to evaluate potential volatile organics contamination from the ambient air arising during sample collection.
- Equipment blanks are samples of an analyte-free matrix that have been used to rinse sampling equipment prior to sampling. The results are used to evaluate contamination arising from contact with sampling equipment, and to verify the effectiveness of equipment decontamination procedures.
- Trip blanks are samples of an analyte-free matrix that have been transported unopened from a controlled area to the sampling site and finally to the laboratory. Trip blanks are used to monitor volatile organics contamination of samples during transport, field handling, and storage.

Duplicate samples are typically collected at a frequency of 10%, or at least once per sampled media. Duplicate samples are best collected at sample points with very high or very low pollutant concentrations. The various blank samples are also typically collected with a combined frequency of approximately 10 percent.

The primary objective of establishing QA/QC procedures is to ensure that data are of the quality necessary to demonstrate that the treatment technologies selected and tested comply with the PFPR rule. Table 6-13 lists the

Table 6-13
Overall Quality Objectives

- Obtain all the critical data necessary to support decision-making;
- Collect representative samples according to the procedures established in the sampling and analysis plan;
- Ensure data comparability by using standard methods and controlled systems to collect and analyze samples; and
- Provide analytical results of known and acceptable precision and accuracy.

overall quality objectives that should be met. Both the facility and the laboratory performing the analyses are responsible for ensuring that the data quality objectives are met.

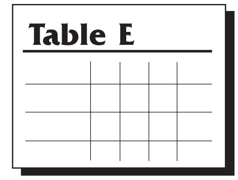


Table E: Summary and Evaluation of Test Results

Following the treatability test, the facility should summarize and evaluate the results to determine whether the test goals were achieved. The facility can use Table E as the starting point for compiling and evaluating the test results, including all analytical data, records of design and operating parameters achieved during the test, and treatability test operator observations. Completing this table will enable facility personnel to assess which treatment technologies were effective in reducing specific constituents in the wastewater, and determine the optimum operating parameters for each treatment unit. Four steps that can be used to evaluate the treatability test results are detailed below.

Treatability Test Goals

- Determine treatment effectiveness;
- Identify analytical parameters to act as surrogates for pesticide active ingredient analyses;
- Identify design and operating parameters to act as indicators for treatment effectiveness;
- Comply with permitting requirements; and
- Optimize treatment performance.

Step 1: Document Test Results

The purpose of the treatment system is to reduce contaminant levels in PFPR wastewaters. The primary constituents of concern for the PFPR industry are the pesticide active ingredients used in the facility's products. Other constituents, such as solvents or inert ingredients, may also be a concern, depending on site-specific criteria.

To evaluate the effectiveness of the treatment system, a facility should first document all test results on Table E. Figure 6-5 is an example of a completed Table E that presents the types of data collected during the treatability test. The unshaded "**Technology**", "**Primary Constituents**", "**Design and Operating Parameters**", and "**Constituent Concentration**" columns illustrate this example. Note that test results can be documented for each technology, as well as for the entire treatment system.

Step 2: Calculate Performance Measures

The effectiveness of a treatment step can be evaluated through performance measures that look at how much contaminant is removed from the wastewater, the amount of other waste generated by the treatment step, and the cost of the treatment. The most common measure of treatment effectiveness is the destruction and removal efficiency (DRE), also known as percent removal, which measures the amount of contaminant removed from the waste stream. In addition to DREs, treatment effectiveness may be measured with technology-specific measures, such as a hydrolysis half-life. These measures are often useful in comparing the results of different treatment tests using the same technology.

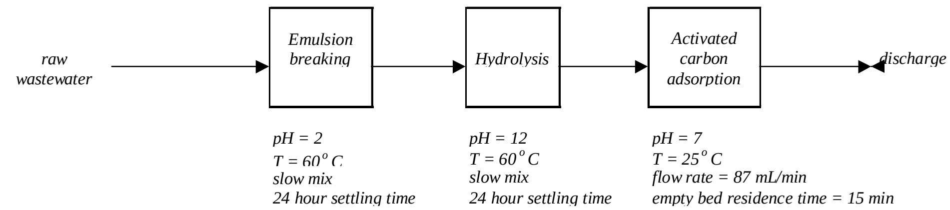
As shown in Figure 6-6, facilities can use the **"Performance Measures"** columns on Table E to document these measures. Once the treatment performance is calculated, facilities can determine whether that technology was successful in removing or destroying that constituent and document the re-

Table E: Summary and Evaluation of Test Results

Facility: ____________________ **Location:** ____________________

Date: ____________________ **Prepared by:** ____________________

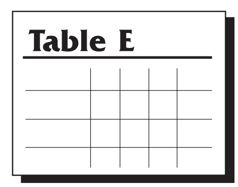
Insert your optimal treatment train and operating parameters in the space provided below:



Technology	Primary Constituents	Design and Operating Parameters: pH	Temperature (°C)	Other Treatment Time	Other Settling Time	Other Reaction Time	Constituent Concentration: Influent (ug/L)	Effluent (ug/L)	Performance Measures[1]: Percent Removal	Other Hydrolysis Half-Life	Effectively Treated? (Y/N)
Emulsion breaking pretest	Sample contained all the emulsion-	2.01	60	1 hour	24 hours		NA	NA			
	breaking constituents except	11.74	60	1 hour	24 hours		NA	NA			
	Linalool and Pyrethrin II.	7	25	1 hour	24 hours		NA	NA			
Emulsion breaking	Cyanazine	2	60	1 hour	24 hours		3,750	714			
	Linalool	Emulsion breaking data for this constituent were not available.					NA	NA			
	Metolachlor	2	60	1 hour	24 hours		15,700	20,400			
	Pendimethalin	2	60	1 hour	24 hours		110	49.0			
	Pyrethrin II	Emulsion breaking data for this constituent were not available.					NA	NA			
	Biological Oxygen Demand (BOD_5)	2	60	1 hour	24 hours		< 108	< 35			
	Hexane Extractable Material (HEM)	2	60	1 hour	24 hours		< 16.5	56.0			
	Total Organic Carbon (TOC)	2	60	1 hour	24 hours		534	534			
	Total Suspended Solids (TSS)	2	60	1 hour	24 hours		334	6.00			
Hydrolysis	Cyanazine	12	60			24 hours	714	< 2			
	Linalool	12	60			24 hours	5,760	792			
	Metolachlor	12	60			24 hours	20,400	14,700			
	Pendimethalin	12	60			24 hours	49.0	45.0			
	Pyrethrin II	12	60			24 hours	81.1	< 5			
	Biological Oxygen Demand (BOD_5)	12	60			24 hours	< 35	45.0			
	Hexane Extractable Material (HEM)	12	60			24 hours	56.0	44.0			
	Total Organic Carbon (TOC)	12	60			24 hours	534	505			
	Total Suspended Solids (TSS)	12	60			24 hours	6.00	303			

[1] NA=not analyzed, NC=not calculated.

Figure 6-5. Documenting Test Results



sults in the last column, **"Effectively Treated?"** A facility should evaluate three measures to determine if the technology effectively removed that constituent:

- Percent removal;
- Final effluent concentration; and
- Minimum detection limit.

For example, if 95% or more of a constituent is removed by a technology, that technology would be considered effective. Conversely, if a technology only removes 30% of a constituent, but the constituent is removed to below its detection limit, the constituent is effectively treated.

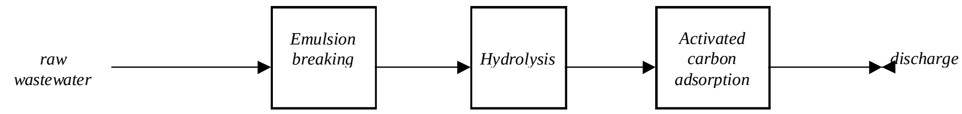
For cost purposes, the facility should also evaluate the technology-specific performance measures. For example, as shown in Figure 6-6, metolachlor is somewhat reduced by the hydrolysis step; however, the half-life is almost 60 hours. Hydrolysis alone would not be a cost-effective treatment technology for metolachlor in this wastewater.

In addition to the DRE calculation, a discussion of several technology-specific measures typically used to evaluate hydrolysis and activated carbon adsorption treatability test results are described below. Requirements for measuring treatment effectiveness for other technologies may be identified through review of technical literature.

Table E: Summary and Evaluation of Test Results

Facility:		**Location:**	
Date:		**Prepared by:**	

Insert your optimal treatment train and operating parameters in the space provided below:



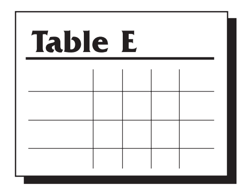
pH = 2	*pH = 12*	*pH = 7*
T = 60° C	*T = 60° C*	*T = 25° C*
slow mix	*slow mix*	*flow rate = 87 mL/min*
24 hour settling time	*24 hour settling time*	*empty bed residence time = 15 min*

Technology	Primary Constituents	Design and Operating Parameters					Constituent Concentration		Performance Measures[1]		Effectively Treated? (Y/N)
		pH	Temperature (°C)	Other Treatment Time	Other Settling Time	Other Reaction Time	Influent (ug/L)	Effluent (ug/L)	Percent Removal	Other Hydrolysis Half-Life	
Emulsion breaking pretest	*Sample contained all the emulsion-*	*2.01*	*60*	*1 hour*	*24 hours*		*NA*	*NA*	*NA*		*excellent*
	breaking constituents except	*11.74*	*60*	*1 hour*	*24 hours*		*NA*	*NA*	*NA*		*good*
	Linalool and Pyrethrin II.	*7*	*25*	*1 hour*	*24 hours*		*NA*	*NA*	*NA*		*minimal*
Emulsion breaking	*Cyanazine*	*2*	*60*	*1 hour*	*24 hours*		*3,750*	*714*	*81.0%*		*Y*
	Linalool	*Emulsion breaking data for this constituent were not available.*					*NA*	*NA*	*NA*		*NA*
	Metolachlor	*2*	*60*	*1 hour*	*24 hours*		*15,700*	*20,400*	*NC*		*N*
	Pendimethalin	*2*	*60*	*1 hour*	*24 hours*		*110*	*49.0*	*55.3%*		*N*
	Pyrethrin II	*Emulsion breaking data for this constituent were not available.*					*NA*	*NA*	*NA*		*NA*
	Biological Oxygen Demand (BOD_5)	*2*	*60*	*1 hour*	*24 hours*		*< 108*	*< 35*	*NC*		*inconclusive*
	Hexane Extractable Material (HEM)	*2*	*60*	*1 hour*	*24 hours*		*< 16.5*	*56.0*	*NC*		*N*
	Total Organic Carbon (TOC)	*2*	*60*	*1 hour*	*24 hours*		*534*	*534*	*NC*		*N*
	Total Suspended Solids (TSS)	*2*	*60*	*1 hour*	*24 hours*		*334*	*6.00*	*98.2%*		*Y*
Hydrolysis	*Cyanazine*	*12*	*60*			*24 hours*	*714*	*< 2*	*> 99.7%*	*2.84*	*Y*
	Linalool	*12*	*60*			*24 hours*	*5,760*	*792*	*75.7%*	*30.8*	*Y*
	Metolachlor	*12*	*60*			*24 hours*	*20,400*	*14,700*	*27.9%*	*59.6*	*N*
	Pendimethalin	*12*	*60*			*24 hours*	*49.0*	*45.0*	*8.16%*	*NC*	*Y*
	Pyrethrin II	*12*	*60*			*24 hours*	*81.1*	*< 5*	*93.8%*	*7.46*	*Y*
	Biological Oxygen Demand (BOD_5)	*12*	*60*			*24 hours*	*< 35*	*45.0*	*NC*	*NA*	*N*
	Hexane Extractable Material (HEM)	*12*	*60*			*24 hours*	*56.0*	*44.0*	*NC*	*NA*	*N*
	Total Organic Carbon (TOC)	*12*	*60*			*24 hours*	*534*	*505*	*17.8%*	*NA*	*N*
	Total Suspended Solids (TSS)	*12*	*60*			*24 hours*	*6.00*	*303*	*NC*	*NA*	*N*

[1] NA=not analyzed, NC=not calculated.

Figure 6-6. Calculating Performance Measures

➡ Destruction and Removal Efficiency Calculation



The DRE is an overall measure of the effectiveness of a treatment. While some technologies, such as hydrolysis and chemical oxidation, destroy contaminants by breaking chemical bonds joining the atoms in a molecule, other technologies, such as activated carbon adsorption and emulsion breaking, remove contaminants by separating the contaminants from the wastewater. Other technologies may use a combination of destruction and removal.

The DRE of a particular technology is based on the sum of the destruction and removal achieved by a technology and does not differentiate between the two. Some facilities may need to differentiate between destruction and removal technologies for practical purposes. Since destruction technologies (e.g., hydrolysis) eliminate a contaminant, they typically do not generate a residue that must be further disposed of, or if they do generate a residue, it is generally of a smaller volume than removal technologies. Removal technologies (e.g., activated carbon adsorption) separate the contaminants from the wastewater, but the separated contaminants then require additional management, such as reuse, recycling, or disposal.

As shown in Figure 6-7, the DRE is equal to the mass of contaminant in the treatment system influent minus the mass of contaminant in the effluent, divided by the mass of contaminant in the influent. This measure may also be referred to as the percent removal when expressed as a percentage.

$$DRE = \frac{(Mass_{influent}) - (Mass_{effluent})}{(Mass_{influent})}$$

Figure 6-7. Destruction and Removal Efficiency Calculation

A mass balance constructed for the treatment system may help facilities identify areas of wastewater and contaminant gain and loss. Constructing a mass balance requires listing all of the influent streams and all of the effluent streams of a system and listing their masses. Using the law of conservation of mass, the total system influent mass should equal the total system effluent mass plus any mass that may have been destroyed through a chemical reaction. If the mass does not balance, then it is likely that some influent or effluent stream (e.g., adsorption to treatment system components or evaporation) has been overlooked. A mass balance can be conducted on individual unit operations or on an entire treatment train; it can also be performed on the entire wastewater volume treated or on one specific contaminant. When the volume of the wastewater does not significantly change during treatment, the DRE can be calculated using the contaminant concentration rather than mass.

Determining the DRE may be difficult if contaminant concentrations are less than the analytical detection limit, or if contaminants in the wastewater interfere with laboratory analysis and cause a high detection limit. Table 6-14 contains some general rules of thumb to follow when estimating the DRE in these circumstances.

When determining treatment efficiency, it may be helpful to calculate DREs for each unit operation as well as for the entire treatment system. Information on DREs for individual unit operations may help facilities identify which unit operations in a treatment train are not performing optimally. In some cases, it may even be possible to exclude individual unit operations from the treatment train if the treatment effectiveness for one particular operation is insignificant.

Table 6-14
Calculation of DREs When Constituents Are Below the Level of Detection

The DRE can be calculated, using the formula in Figure 6-7, if the following conditions apply:

- Both the influent and effluent concentrations are greater than the reported detection limits, and the influent concentration is greater than the effluent concentration; and
- The influent concentration is greater than the reported detection limit, and the effluent concentration is less than the reported detection limit. The DRE can be calculated using the reported detection limit for the effluent concentration in the calculation in Figure 6-7. The percent removals calculated should be shown in the test report with the “greater than” (“>”) symbol.

The DRE cannot be calculated if the following conditions apply:

- Both the influent and effluent concentrations are greater than the reported detection limits, and the influent concentration is less than the effluent concentration;
- The influent concentration is less than the reported detection limit, and the effluent concentration is detected; and
- Both the influent and effluent concentrations are less than the reported detection limits.

➡ Hydrolysis Half-Life Calculation

Hydrolysis is an aqueous chemical reaction in which a molecule is broken into two or more organic molecules. Hydrolysis of most pesticide active ingredients takes place at an elevated pH and temperature, although some pesticides may be amenable to acid hydrolysis.

To evaluate the effectiveness of hydrolysis on PFPR wastewater, half-lives are typically calculated for each pesticide active ingredient. The hydrolysis half-life is defined as the time required for the reactant concentration to decrease to half the initial concentration. When hydrolysis occurs in alkaline conditions (e.g., pH = 12), the reaction can be modeled with a first-order rate equation, as shown in Figure 6-8.

$$t_{1/2} = \frac{\ln (2)}{k_1}$$

$t_{1/2}$ = *half-life (minutes)*
k_1 = *pseudo first-order rate constant (minutes^{-1})*

Figure 6-8. Hydrolysis Half-Life Equation

For alkaline hydrolysis, the half-life is determined using the procedure detailed in Table 6-15. For further information on hydrolysis rate reactions and the calculation of half-lives under different treatment conditions, consult a hydrolysis text or see the references listed at the end of Chapter 5.

Table 6-15
Alkaline Hydrolysis Half-Life Determination

1) Plot the natural logarithm of the constituent concentration versus time.
2) Draw a trend line to linearly fit the data.
3) Calculate the slope of the line, which is equal to the hydrolysis rate constant, k_1.
4) Calculate the half-life using the equation in Figure 6-8.

➡ Activated Carbon Adsorption Performance Measures

Activated carbon adsorption is a treatment technology that removes certain organic constituents from wastewater through physical and chemical forces that bind the constituents to the carbon surface. The adsorption of pesticide active ingredients typically takes place at neutral pH and ambient temperatures. Two performance measures are used to evaluate the effectiveness of activated carbon adsorption on PFPR wastewater: carbon saturation loadings and carbon breakthrough curves.

The carbon saturation loading is the mass of organic constituents that can be adsorbed onto a unit mass of activated carbon. As wastewater is processed through a carbon bed, organic constituents are adsorbed onto the activated carbon. At the same time, other constituents may be desorbed from the carbon. When the rate of sorption and desorption reach equilibrium, the carbon is said to be saturated, and no further removal of organic constituents is achieved.

The saturation loading varies with the concentration of the compounds being adsorbed, the wastewater pH and temperature, and the presence of other adsorbable compounds. A carbon adsorption isotherm is typically constructed to show the relationship between the saturation loading and the pollutant equilibrium concentration at a given temperature. This information can be used to determine how much carbon is necessary to remove a constituent to a set effluent concentration. Figure 6-9 presents an example of a carbon adsorption isotherm for metolachlor, a pesticide active ingredient.

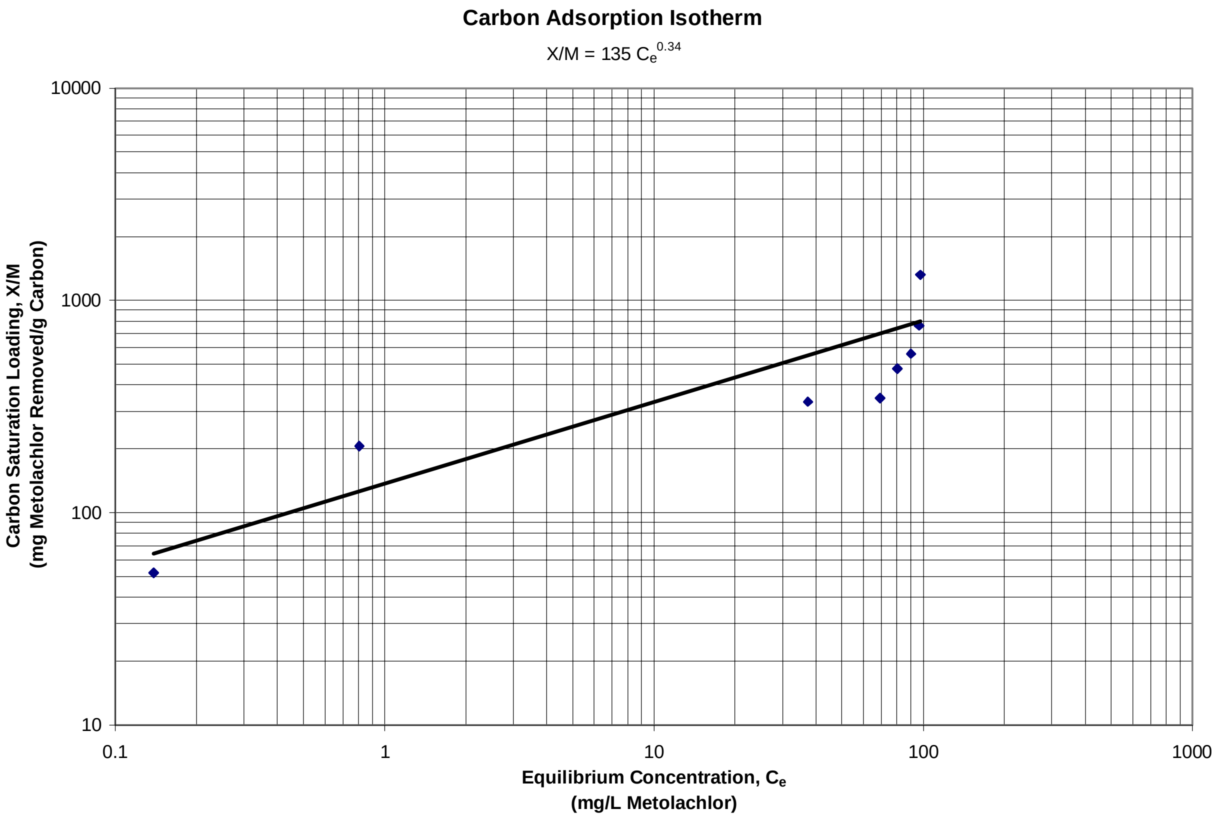


Figure 6-9. Carbon Adsorption Isotherm.

Carbon isotherms can be found in literature for many pesticide active ingredients; however, a facility may also conduct a separate treatability test to construct their own isotherms, since precise saturation loadings are specific to a facility's individual wastewater stream. One experimental technique for determining saturation loadings is presented in *Carbon Adsorption Isotherms for Toxic Organics,* listed in the references at the end of Chapter 5. For further information on activated carbon treatment and the construction of adsorption isotherms, consult a wastewater treatment text or see the references listed at the end of Chapter 5.

Carbon breakthrough curves are another useful measure of the performance of an activated carbon system. Breakthrough curves are often used to estimate how much wastewater can be treated through an activated carbon unit before it is necessary to replace or regenerate the activated carbon. The curve is constructed by plotting contaminant concentration in the effluent versus volume of wastewater treated. When wastewater is first treated through a bed of fresh carbon, the concentration of contaminant in the effluent is at a minimum level. At some later time during treatment, the carbon becomes saturated and the contaminant is no longer adsorbed completely. The concentration of the contaminant in the effluent increases as more wastewater passes through the unit and more of the available pore space in the carbon becomes filled with contaminant. At the point where no additional contaminant is being adsorbed, the carbon is said to be exhausted. Figure 6-10 presents an example of a breakthrough curve for a general pesticide active ingredient. As seen in this example, carbon breakthrough occurred after about 10 liters of wastewater were treated through the carbon bed.

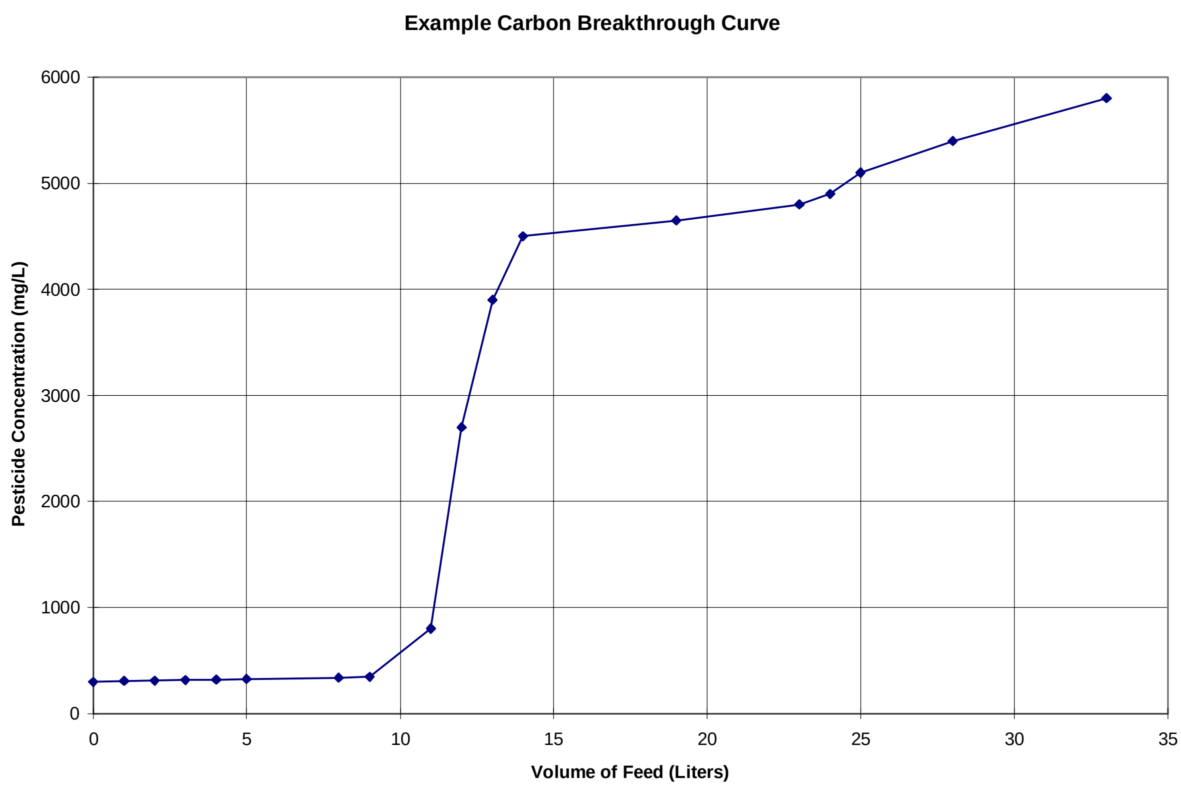


Figure 6-10. Carbon Breakthrough Curve

Step 3: Compare Treatment Technology Results

To identify the most appropriate treatment train, the facility needs to compare the results of their treatability tests to previous treatability tests, either conducted by the facility or contained in the technical literature. The facility may wish to consider aspects other than overall treatment effectiveness, including cost, reliability, residuals generated, and need for highly skilled operators. When comparing treatability tests conducted using the same technology, the comparison is more straightforward than when comparing treatability tests using different technologies.

When comparing the same technologies, the facility can evaluate treatment effectiveness measures, such as effluent concentrations and DREs, but they can also compare technology-specific measures, such as hydrolysis half-lives. The facility may also be able to compare factors other than treatment effectiveness (e.g., reliability and cost) more directly.

When comparing different technologies, the comparisons may be more difficult. Although the facility can still compare final effluent concentrations and DREs, technology-specific criteria are not directly comparable. In addition, it may be more difficult to compare technologies on bases other than treatment effectiveness, such as reliability and cost.

Facilities should exercise caution when comparing test results from different wastewaters. Because of the high degree of variability of PFPR wastewaters, treatment that is effective on some wastewaters might not be effective on other wastewaters that are similar. For example, two separate facilities have metolachlor in their wastewater, but one facility has a low TOC loading in their wastewater, while the second facility has a high TOC loading. Activated carbon may effectively remove the metolachlor from the wastewater with low TOC levels; however, the wastewater with high TOC levels may have other organic constituents that compete with the metolchlor for adsorption, resulting in reduced removal of metolachlor.

Therefore, when comparing treatability test results from different facilities, from EPA-sponsored treatability tests, or from technical literature, facilities should take into account how their wastewater differs from the wastewater tested. Differences in contaminant concentrations, combinations of contaminants, and levels of suspended solids, dissolved solids, TOC, surfactants, detergents, and solvents may cause wastewater differences that can affect the performance, cost, and/or reliability of a treatment technology.

Step 4: Evaluate Cost-Effectiveness of Treatment

As discussed in Step 3, facilities should compare the treatment technology test results to choose the technology(ies) that will treat their wastewater to the level required to comply with the final rule and that will be the most cost-effective for them to use. In determining cost-effectiveness, facilities need to examine factors such as the cost of installing new technologies and the annual operation and maintenance costs for those technologies, as well as whether the technologies will meet the regulatory requirements of the rule.

In evaluating the cost-effectiveness of different treatment technologies, facilities should consider whether wastewater treatment is the most cost-effective method for them to comply with the rule. One of the factors that should be taken into consideration is the volume of wastewater generated. A facility may be able to treat its wastewater adequately using available technologies; however, because the facility's volume of wastewater is so small, it may be less expensive for the facility to dispose of the wastewater off site than to install a treatment system.

After conducting the treatability test to determine the most effective treatment method, the facility may determine that the technologies they have tested and compared simply are not cost-effective. For example, the facility has determined through treatabilty testing that its floor wash water can be adequately treated using activated carbon adsorption, preceded by an emulsion breaking pretreatment step. However, the cost of installing and operating this treatment train is more than what the facility would pay to have the floor wash water contract hauled off site for disposal. In this case, it would be more cost-effective for the facility to segregate its floor wash water and store it until it can be transferred for off-site disposal. Note that cost-effectiveness may not be the only factor considered by facilities when choosing to install treatment or contract off site for disposal. Some facilities may choose to limit the possible cross-media impacts associated with off-site disposal.

As discussed in Chapter 4, the facility can use Table C to reach a preliminary decision on how to comply with the final rule for each wastewater stream (i.e., zero discharge or wastewater treatment and discharge after implementing approved P2 practices). For those wastewater streams for which the facility chose the P2 alternative and that would require treatment prior to discharge, the facility now has the information necessary to make the final compliance choice. In some cases, the facility may change its preliminary compliance decision from the P2 alternative (including on-site wastewater treatment) to contract hauling of its wastewater, based on its evaluation of its wastewater treatment options. The final compliance decision and Table C are discussed in more detail in the on-site compliance paperwork section of Chapter 7.

Step 5: Prepare the Test Report

For each treatability test, facilities should prepare a final test report that presents the information gathered during the test and the analysis of test results. The report can serve as documentation of the test and as a reference for future testing.

Test Report Components

- Recorded design and operating parameters;
- Observations made by treatability test personnel;
- Deviations from the sampling and analysis plan;
- Analytical results; and
- Calculations of DREs and other treatment criteria.

As mentioned previously in this chapter, Tables D and E can be used by facilities to identify the wastewaters and contaminants that will be treated at the facility and the treatment technologies within the facility's treatment train that are expected to treat each contaminant. Many facilities will find it helpful to use a block diagram to draw each treatment step of a treatment train. In such a diagram, facilities can list the influent wastewater streams to each unit operation in a treatment train, the contaminants within each wastewater stream, and the contaminants treated within each unit operation block.

Tables D and E can also be used as compliance documentation to show that appropriate treatment technologies are being used to treat each wastewater stream. Chapter 7 discusses in detail the documentation needed to show compliance with the final rule.